

Claims:

1. A pre-mix for a syntactic phenolic foam composition, the premix comprising

5 thermoplastic microspheres selected from the group comprising thermally expandable microspheres and thermally expanded microspheres, the microspheres comprising a thermoplastic polymer shell made of a homopolymer or copolymer of 100 to 25, for example 93 to 40, parts by weight of a nitrile-containing, ethylenically unsaturated monomer, or a mixture thereof; and 0 to 75, for example
10 7 to 60, parts by weight of a non-nitrile-containing, ethylenically unsaturated monomer, or a mixture thereof; and a propellant, or a mixture thereof, trapped within the thermoplastic polymer shell;

and one of either
15 a highly reactive phenolic resole resin capable of fully crosslinking at temperatures between 15°C and 25°C, optionally in the presence of up to ten times its own weight in water, and having, typically, a free phenol content of 12-15% (w/w);
20 or

an acidic catalyst for curing the phenolic resole resin.
- 25 2. The pre-mix of claim 1, in which the highly reactive phenolic resole resin is obtainable by reacting a substituted or unsubstituted phenol and an aldehyde, preferably formaldehyde, in the presence of an alkaline catalyst, preferably sodium hydroxide, at a temperature of no more than 65°C, preferably no more than 60±2°C, more preferably no more than about 60°C before neutralisation
30 of the catalyst.

3. The pre-mix of claim 1 or 2, in which the phenolic resole resin has a molecular weight of no greater than 1000 daltons.
- 5 4. The pre-mix of claim 1, in which the acidic catalyst is selected from the group comprising a strong organic acid, an ester of a strong organic acid, a weak inorganic acid, an ester of a weak inorganic acid, and a mixture thereof, preferably from the group comprising a weak inorganic acid, an ester of a weak inorganic acid and a mixture thereof, more preferably from the group comprising a
10 phosphate ester, phosphoric acid and a mixture thereof.
5. The pre-mix of claim 4, in which the acidic catalyst additionally comprises a strong organic acid, preferably *p*-toluene sulphonic acid.
- 15 6. The pre-mix of claim 1, in which the at least one nitrile-containing ethylinically unsaturated monomer is selected from the group comprising acrylonitrile, methacrylonitrile, α -chloroacrylonitrile, α -ethoxyacrylonitrile, fumaroacrylonitrile, crotoacrylonitrile and a mixture thereof, of which acrylonitrile or methacrylate is preferred.
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7. The pre-mix of claim 1, in which the at least one non-nitrile-containing, ethylinically unsaturated monomer is selected from the group comprising of acrylic esters, methacrylic esters, vinyl chloride, vinylidene chloride, vinylidene dichloride, vinyl pyridine, vinyl esters, styrenes and derivatives and
25 mixtures thereof, of which vinylidene chloride and / or vinyl chloride are preferred.
8. The pre-mix of claim 1, in which the propellant is a volatile liquid selected from the group comprising short chain alkanes and isoalkanes and mixtures, preferably selected from the group comprising isopentane, isobutane, n-
30 butane, pentane and a mixture thereof.

9. A syntactic phenolic foam composition comprising

a highly reactive phenolic resole resin capable of fully crosslinking at

5 temperatures between 15°C and 25°C, optionally in the presence of up to ten times its own weight in water, and having, typically, a free phenol content of 12-15% (w/w);

an acidic catalyst for curing the phenolic resole resin; and

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thermoplastic microspheres selected from the group comprising thermally expandable microspheres and thermally expanded microspheres, the microspheres comprising a thermoplastic polymer shell made of a homopolymer or copolymer of 100 to 25, for example 93 to 40, parts by weight of a nitrile-containing, ethylenically unsaturated monomer, or a mixture thereof; and 0 to 75, for example 7 to 60, parts by weight of a non-nitrile-containing, ethylenically unsaturated monomer, or a mixture thereof; and a propellant, or a mixture thereof, trapped within the thermoplastic polymer shell.

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20 10. The syntactic phenolic foam composition of claim 9, in which the highly reactive phenolic resole resin is obtainable by reacting a substituted or unsubstituted phenol and an aldehyde, preferably formaldehyde, in the presence of an alkaline catalyst, preferably sodium hydroxide, at a temperature of no more than 65°C, preferably no more than 60±2°C, more preferably no more than about 60°C.

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11. The syntactic phenolic foam composition of claim 9 or 10, in which the phenolic resole resin has a molecular weight of no greater than 1000 daltons.

30 12. The syntactic phenolic foam composition of claim 9 or 10, in which the acidic catalyst is selected from the group comprising a strong organic acid, an

ester of a strong organic acid, a weak inorganic acid, an ester of a weak inorganic acid, and a mixture thereof, preferably from the group comprising a weak inorganic acid, an ester of a weak inorganic acid and a mixture thereof, more preferably from the group comprising a phosphate ester, phosphoric acid and a mixture thereof.

13. The syntactic phenolic foam composition of claim 12, in which the acidic catalyst additionally comprises a strong organic acid, preferably *p*-toluene sulphonic acid.

14. The syntactic phenolic foam composition of claim 9, in which the at least one nitrile-containing ethylinically unsaturated monomer is selected from the group comprising acrylonitrile, methacrylonitrile, α -chloroacrylonitrile, α -ethoxyacrylonitrile, fumaroacrylonitrile, crotoacrylonitrile and a mixture thereof, of which acrylonitrile or methacrylate is preferred.

15. The syntactic phenolic foam composition of claim 9, in which the at least one non-nitrile-containing, ethylinically unsaturated monomer is selected from the group comprising acrylic esters, methacrylic esters, vinyl chloride, vinylidene chloride, vinylidene dichloride, vinyl pyridine, vinyl esters, styrenes and derivatives and mixtures thereof, of which vinylidene chloride and / or vinyl chloride are preferred.

16. The syntactic phenolic foam composition of claim 9, in which the propellant is a volatile liquid selected from the group comprising short chain alkanes and isoalkanes and mixtures thereof, preferably from the group comprising isopentane, isobutane, n-butane, pentane and a mixture thereof.

17. A process for preparing the syntactic phenolic foam composition of claim 8, the process comprising either curing the pre-mix of claim 1 in the presence of the other of the

the acidic catalyst for curing the phenolic resole resin;

or

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the highly reactive phenolic resole resin capable of fully crosslinking at temperatures between 15°C and 25°C, optionally in the presence of up to ten times its own weight in water, and having, typically, a free phenol content of 12-15% (w/w); or

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curing a highly reactive phenolic resole resin capable of fully crosslinking at temperatures between 15°C and 25°C, optionally in the presence of up to ten times its own weight in water, and having, typically, a free phenol content of 12-15% (w/w);

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an acidic catalyst for curing the phenolic resole resin; and

thermoplastic microspheres, the microspheres being selected from the group comprising thermally expandable microspheres and thermally expanded microspheres, the microspheres comprising a thermoplastic polymer shell made of
20 a homopolymer or copolymer of 100 to 25, for example 93 to 40, parts by weight of a nitrile-containing, ethylenically unsaturated monomer, or a mixture thereof; and 0 to 75, for example 7 to 60, parts by weight of a non-nitrile-containing, ethylenically unsaturated monomer, or a mixture thereof; and a propellant, or a mixture thereof, trapped within the thermoplastic polymer shell.

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18. The process of claim 17, in which the highly reactive phenolic resole resin is obtainable by reacting a substituted or unsubstituted phenol and an aldehyde, preferably formaldehyde, in the presence of an alkaline catalyst, preferably sodium hydroxide, at a temperature of no more than 65°C, preferably no more
30 than 60±2°C, more preferably no more than about 60°C.

19. The process of claim 17 or 18, in which the phenolic resole resin has a molecular weight of no greater than 1000 daltons.
20. The process of claim 17, in which the acidic catalyst is selected from the group comprising a strong organic acid, an ester of a strong organic acid, a weak inorganic acid, an ester of a weak inorganic acid, and a mixture thereof, preferably from the group comprising a weak inorganic acid, an ester of a weak inorganic acid and a mixture thereof, more preferably from the group comprising a phosphate ester, phosphoric acid and a mixture thereof.
21. The process of claim 20, in which the acidic catalyst additionally comprises a strong organic acid, preferably *p*-toluene sulphonic acid.
22. The process of claim 17, in which the at least one nitrile-containing ethylinically unsaturated monomer is selected from the group comprising acrylonitrile, methacrylonitrile, α -chloroacrylonitrile, α -ethoxyacrylonitrile, fumaroacrylonitrile, crotoacrylonitrile and a mixture thereof, of which acrylonitrile or methacrylate is preferred.
23. The process of claim 17, in which the at least one non-nitrile-containing, ethylinically unsaturated monomer is selected from the group comprising of acrylic esters, methacrylic esters, vinyl chloride, vinylidene chloride, vinylidene dichloride, vinyl pyridine, vinyl esters, styrenes and derivatives and mixtures thereof, of which vinylidene chloride and / or vinyl chloride are preferred.
24. The process of claim 17, in which the propellant is a volatile liquid selected from the group comprising short chain alkanes and isoalkanes and mixtures thereof, preferably from the group comprising isopentane, isobutane, n-butane, pentane and a mixture thereof.